

IN THE SPECIFICATION

At page 6, line 5, please enter the following:

Documents

S. R. Pollack and C. E. Morris, "Tunneling through gaseous oxidized films of Al_2O_3 ," Trans. AIME, Vol. 233, p. 497, 1965.

T. P. Ma et al., "Tunneling leakage current in ultrathin (<4 nm) nitride/oxide stack dielectrics," IEEE Electron Device Letters, vol. 19, no. 10, pp. 388-390, 1998.

O. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys", Butterworth, London, pp. 53-64, 1962.

J. M. Eldridge and J. Matisoo, "Measurement of tunnel current density in a Metal-Oxide-Metal system as a function of oxide thickness," Proc. 12th Intern. Conf. on Low Temperature Physics, pp. 427-428, 1971.

J. M. Eldridge and D. W. Dong, "Growth of thin PbO layers on lead films. I. Experiment," Surface Science, Vol. 40, pp. 512-530, 1973.

J. H. Greiner, "Oxidation of lead films by rf sputter etching in an oxygen plasma", J. Appl. Phys., Vol. 45, No. 1, pp. 32-37, 1974.

J. M. Eldridge and J. Matisoo, entitled "Measurement of tunnel current density in a Metal-Oxide-Metal system as a function of oxide thickness," Proc. 12th Intern. Conf. on Low Temperature Physics, pp. 427-428, 1971.

S. M. Sze, Physics of Semiconductor Devices, Wiley, NY, pp. 553-556, 1981.

G. Simmons and A. El-Badry, "Generalized formula for the electric tunnel effect between similar electrodes separated by a thin insulating film," J. Appl. Phys., Vol. 34, p. 1793, 1963.

S. R. Pollack and C. E. Morris, "Tunneling through gaseous oxidized films of Al_2O_3 ," Trans. AIME, Vol. 233, p. 497, 1965,

Z. Hurych, "Influence of nonuniform thickness of dielectric layers on capacitance and tunnel currents," Solid-State Electronics, Vol. 9, p. 967, 1966.

S. P. S. Arya and H. P. Singh, "Conduction properties of thin Al_2O_3 films," Thin Solid Films, Vol. 91, No. 4, pp. 363-374, May 1982.

K.-H. Gundlach and J. Holzl, "Logarithmic conductivity of Al-Al₂O₃-Al tunneling junctions produced by plasma- and by thermal-oxidation", surface Science, Vol. 27, pp. 125-141, 1971.

J. Grimblot and J. M. Eldridge, "I. Interaction of Al films with O₂ at low pressures", J. Electro. Chem. Soc., Vol. 129, No. 10, pp. 2366-2368, 1982.

J. Grimblot and J. M. Eldridge, "II. Oxidation of Al films", ibid, 2369-2372, 1982.

J. M. Greiner, "Josephson tunneling barriers by rf sputter etching in an oxygen plasma," J. Appl. Phys., Vol. 42, No. 12, pp. 5151-5155, 1971.

O. Michikami et al., "Method of fabrication of Josephson tunnel junctions," U.S. Pat. 4,412,902, Nov. 1, 1983.

H. F. Luan et al., "High quality Ta₂O₅ gate dielectrics with T_{ox,eq} <10 angstroms," IEDM Tech. Digest, pp. 141-144, 1999.

Hase et al., "Method of manufacturing an oxide superconducting film," U.S. Pat. 5,350,738, Sept. 27, 1994.

Please amend the paragraph beginning at page 21, line 10 as follows:

As shown in Figure 7B, the electric field is determined by the total voltage difference across the structure, the ratio of the capacitances (see Figure 7A), and the thickness of the interpoly dielectric 707.

$$t_{ig} = \frac{\epsilon_2 t_{ox}}{\epsilon_1}$$

The voltage across the interpoly dielectric 707 will be, $\Delta V_2 = V C_1 / (C_1 + C_2)$, where ΔV is the total applied voltage. The capacitances, C , of the structures depends on the dielectric constant, ϵ_r , the permittivity of free space, ϵ_0 , and the thickness of the insulating layers, t , and area, A , such that $C = \epsilon_r \epsilon_0 A / t$, Farads/cm². The electric field across the interpoly dielectric insulator 707, having capacitance, C_2 , will then be $E_2 = \Delta V_2 / t_2$, where t_2 is the thickness of this layer.

Please amend the paragraph beginning at page 21, line 19 as follows:

The tunneling current in erasing charge from the floating gate 705 by tunneling to the control gate 713 will then be as shown in Figure 7B given by an equation of the form:

$$J = B \exp(-E_0/E)$$

$$J = \frac{q^2 E^2}{4\pi h \Phi} e^{-E_0/E} \quad E_0 = \frac{8\pi}{3} \frac{\sqrt{2mq\Phi^*}^{3/2}}{h}$$

where E is the electric field across the interpoly dielectric insulator 707 and E₀ depends on the barrier height. Practical values of current densities for aluminum oxide which has a current density of 1 A/cm² at a field of about E = 1V/20Å = 5x10⁺⁶ V/cm are evidenced in a description by Pollack. ~~(See generally, S. R. Pollack and C. E. Morris, "Tunneling through gaseous oxidized films of Al₂O₃," Trans. AIME, Vol. 233, p. 497, 1965).~~ Practical current densities for silicon oxide transistor gate insulators which has a current density of 1 A/cm² at a field of about E = 2.3V/23Å = 1x10⁺⁷ V/cm are evidenced in a description by T. P. Ma et al. ~~(See generally, T. P. Ma et al., "Tunneling leakage current in ultrathin (<4 nm) nitride/oxide stack dielectrics," IEEE Electron Device Letters, vol. 19, no. 10, pp. 388-390, 1998).~~

Please amend the paragraph beginning at page 23, line 6 as follows:

(iii) The oxide growth rate and limiting thickness will increase with oxidation temperature and oxygen pressure. The oxidation kinetics of a metal may, in some cases, depend on the crystallographic orientations of the very small grains of metal which comprise the metal film ~~(see generally, O. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys", Butterworth, London, pp. 53-64, 1962).~~ If such effects are significant, the metal deposition process can be modified in order to increase its preferred orientation and subsequent oxide thickness and tunneling uniformity. To this end, use can be made of the fact that metal films strongly prefer to grow during their depositions having their lowest free energy planes parallel to the film surface. This preference varies with the crystal structure of the metal. For example, fcc metals prefer to form {111} surface plans. Metal orientation effects, if present, would be larger when only a

limited fraction of the metal will be oxidized and unimportant when all or most of the metal is oxidized.

Please amend the paragraph beginning at page 23, line 27 as follows:

This oxide barrier has been studied in detail using Pb/PbO/Pb structures. The oxide itself can be grown very controllably on deposited lead films using either thermal oxidation (~~see generally, J. M. Eldridge and J. Matisoo, "Measurement of tunnel current density in a Metal-Oxide-Metal system as a function of oxide thickness," Proc. 12th Intern. Conf. on Low Temperature Physics, pp. 427-428, 1971; J. M. Eldridge and D. W. Dong, "Growth of thin PbO layers on lead films. I. Experiment," Surface Science, Vol. 40, pp. 512-530, 1973~~) or rf sputter etching in an oxygen plasma (~~see generally, J. H. Greiner, "Oxidation of lead films by rf sputter etching in an oxygen plasma", J. Appl. Phys., Vol. 45, No. 1, pp. 32-37, 1974~~). It will be seen that there are a number of possible variations on this structure. Starting with a clean poly-Si substrate, one processing sequence using thermal oxidation involves:

Please amend the paragraph beginning at page 24, line 18 as follows:

(iii) Using a "low temperature oxidation process" to grow an oxide film of self-limited thickness. In this case, oxygen gas is introduced at the desired pressure in order to oxidize the lead *in situ* without an intervening exposure to ambient air. For a fixed oxygen pressure and temperature, the PbO thickness increases with log(time). Its thickness can be controlled via time or other parameters to *within 0.10 Å*, as determined via *in situ* ellipsometric or *ex situ* measurements of Josephson tunneling currents. This control is demonstrated by the very limited statistical scatter of the current PbO thickness data shown in the insert of Fig. 3 in an article by ~~J. M. Eldridge and J. Matisoo, entitled "Measurement of tunnel current density in a Metal-Oxide-Metal system as a function of oxide thickness," Proc. 12th Intern. Conf. on Low Temperature Physics, pp. 427-428, 1971~~. This remarkable degree of control over tunnel current is due to the excellent control over PbO thickness that can be achieved by "low temperature oxidation." For example, increasing the oxidation time from 100 to 1,000 minutes at an oxygen pressure of 750

Torr at 25C only raises the PbO thickness by 3 Å (e.g., from ~21 to 24 Å), ~~see Fig. 1 in J. M. Eldridge and J. Matisoo, "Measurement of tunnel current density in a Metal Oxide Metal system as a function of oxide thickness," Proc. 12th Intern. Conf. on Low Temperature Physics, pp. 427-428, 1971).~~ Accordingly, controlling the oxidation time to within 1 out of a nominal 100 minute total oxidation time provides a thickness that is within 0.1 Å of 21 Å. The PbO has a highly stoichiometric composition throughout its thickness, as evidenced from ellipsometry ~~(e.g., see Fig. 6 in J. M. Eldridge and D. W. Dong, "Growth of thin PbO layers on lead films. I. Experiment," Surface Science, Vol. 40, pp. 512-530, 1973)~~ and the fact that the tunnel barrier heights are identical for Pb/PbO/Pb structures.

Please amend the paragraph beginning at page 26, line 1 as follows:

A number of studies have dealt with electron tunneling in Al/Al₂O₃/Al structures where the oxide was grown by "low temperature oxidation" in either molecular or plasma oxygen ~~(see generally, S. M. Sze, Physics of Semiconductor Devices, Wiley, NY, pp. 553-556, 1981; G. Simmons and A. El-Badry, "Generalized formula for the electric tunnel effect between similar electrodes separated by a thin insulating film," J. Appl. Phys., Vol. 34, p. 1793, 1963; S. R. Pollack and C. E. Morris, "Tunneling through gaseous oxidized films of Al₂O₃," Trans. AIME, Vol. 233, p. 497, 1965; Z. Hurrych, "Influence of nonuniform thickness of dielectric layers on capacitance and tunnel currents," Solid State Electronics, Vol. 9, p. 967, 1966; S. P. S. Arya and H. P. Singh, "Conduction properties of thin Al₂O₃ films," Thin Solid Films, Vol. 91, No. 4, pp. 363-374, May 1982; K. H. Gundlach and J. Holz, "Logarithmic conductivity of Al-Al₂O₃-Al tunneling junctions produced by plasma and by thermal oxidation," surface Science, Vol. 27, pp. 125-141, 1971).~~ Before sketching out a processing sequence for these tunnel barriers, note:

Please amend the paragraph beginning at page 26, line 19 as follows:

(ii) Tunnel currents are asymmetrical in this system with somewhat larger currents flowing when electrons are injected from Al/Al₂O₃ interface developed during oxide growth. This asymmetry is due to a minor change in composition of the growing oxide: there is a small concentration of excess metal in the Al₂O₃, the concentration of which diminishes as the oxide is grown thicker. The excess Al³⁺ ions produce a space charge that lowers the tunnel barrier at the

inner interface. The oxide composition at the outer $\text{Al}_2\text{O}_3/\text{Al}$ contact is much more stoichiometric and thus has a higher tunnel barrier. *In situ* ellipsometer measurements on the thermal oxidation of Al films deposited and oxidized *in situ* support this model (~~see generally, J. Grimblot and J. M. Eldridge, "I. Interaction of Al films with O_2 at low pressures", J. Electrochem. Soc., Vol. 129, No. 10, pp. 2366-2368, 1982. J. Grimblot and J. M. Eldridge, "II. Oxidation of Al films", *ibid*, 2369-2372, 1982~~). In spite of this minor complication, Al/ Al_2O_3 /Al tunnel barriers can be formed that will produce predictable and highly controllable tunnel currents that can be ejected from either electrode. The magnitude of the currents are still primarily dominated by Al_2O_3 thickness which can be controlled via the oxidation parametrics.

Please amend the paragraph beginning at page 27, line 7 as follows:

With this background, we can proceed to outline one process path out of several that can be used to form Al_2O_3 tunnel barriers. Here the aluminum is thermally oxidized although one could use other techniques such as plasma oxidation (~~see generally, S. R. Pollack and C. E. Morris, "Tunneling through gaseous oxidized films of Al_2O_3 ", Trans. AIME, Vol. 233, p. 497, 1965; K. H. Gundlach and J. Holzl, "Logarithmic conductivity of Al- Al_2O_3 -Al tunneling junctions produced by plasma and by thermal oxidation", Surface Science, Vol. 27, pp. 125-141, 1971~~) or rf sputtering in an oxygen plasma (~~see generally, J. H. Greiner, "Oxidation of lead films by rf sputter etching in an oxygen plasma", J. Appl. Phys., Vol. 45, No. 1, pp. 32-37, 1974~~). For the sake of brevity, some details noted above will not be repeated. The formation of the Al/ Al_2O_3 /Al structures will be seen to be simpler than that described for the Pb/PbO/Pb junctions owing to the much higher melting point of aluminum, relative to lead.

Please amend the paragraph beginning at page 28, line 11 as follows:

Single layers of Ta_2O_5 , TiO_2 , ZrO_2 , Nb_2O_5 and similar transition metal oxides can be formed by "low temperature oxidation" of numerous Transition Metal (e.g., TM oxides) films in molecular and plasma oxygen and also by rf sputtering in an oxygen plasma. The thermal oxidation kinetics of these metals have been studied for decades ~~with numerous descriptions and references to be found in the book by Kubaschewski and Hopkins (O. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys", Butterworth, London, pp. 53-64, 1962)~~. In essence,

such metals oxidize via logarithmic kinetics to reach thicknesses of a few to several tens of angstroms in the range of 100 to 300C. Excellent oxide barriers for Josephson tunnel devices can be formed by rf sputter etching these metals in an oxygen plasma (~~see generally, J. M. Greiner, "Josephson tunneling barriers by rf sputter etching in an oxygen plasma," J. Appl. Phys., Vol. 42, No. 12, pp. 5151-5155, 1971; O. Michikami et al., "Method of fabrication of Josephson tunnel junctions," U.S. Pat. 4,412,902, Nov. 1, 1983~~). Such "low temperature oxidation" approaches differ considerably from MOCVD processes used to produce these TM oxides. MOCVD films require high temperature oxidation treatments to remove carbon impurities, improve oxide stoichiometry and produce recrystallization. Such high temperature treatments also cause unwanted interactions between the oxide and the underlying silicon and thus have necessitated the introduction of interfacial barrier layers. ~~See, for example, H. F. Luan et al., "High quality Ta₂O₅ gate dielectrics with T_{ox,eq} < 10 angstroms," IEDM Tech. Digest, pp. 141-144, 1999.~~

Please amend the paragraph beginning at page 29, line 3 as follows:

A new approach was described in a copending application by J. M. Eldridge, entitled "Thin Dielectric Films for DRAM Storage Capacitors," patent application Serial No. 09/651,380 filed Aug. 29, 2000 (now U.S. Patent No. 6,461,931 and assigned to Micron Technology, Inc.) that utilizes "low temperature oxidation" to form duplex layers of TM oxides. Unlike MOCVD films, the oxides are very pure and stoichiometric as formed. They do require at least a brief high temperature (est. 700 to 800C but may be lower) treatment to transform their microstructures from amorphous to crystalline and thus increase their dielectric constants to the desired values (> 20 or so). Unlike MOCVD oxides, this treatment can be carried out in an inert gas atmosphere, thus lessening the possibility of inadvertently oxidizing the poly-Si floating gate. While this earlier disclosure was directed at developing methods and procedures for producing high dielectric constant films for storage cells for DRAMs, the same teachings can be applied to producing thinner metal oxide tunnel films for the flash memory devices described in this disclosure. The dielectric constants of these TM oxides are substantially greater (>25 to 30 or more) than those of PbO and Al₂O₃. Duplex layers of these high dielectric constant oxide films are easily fabricated with simple tools and also provide improvement in device yields and

reliability. Each oxide layer will contain some level of defects but the probability that such defects will overlap is exceedingly small. Effects of such duplex layers were first reported by one J. M. Eldridge of the present authors and are well known to practitioners of the art. It is worth mentioning that highly reproducible TM oxide tunnel barriers can be grown by rf sputtering in an oxygen ambient, as referenced above (~~see generally, J. M. Greiner, "Josephson tunneling barriers by rf sputter etching in an oxygen plasma," J. Appl. Phys., Vol. 42, No. 12, pp. 5151-5155, 1971; O. Michikami et al., "Method of fabrication of Josephson tunnel junctions," U.S. Pat. 4,412,902, Nov. 1, 1983~~). Control over oxide thickness and other properties in these studies were all the more remarkable in view of the fact that the oxides were typically grown on thick (e.g., 5,000 Å) metals such as Nb and Ta. In such metal-oxide systems, a range of layers and suboxides can also form, each having their own properties. In the present disclosure, control over the properties of the various TM oxides will be even better since we employ very limited (perhaps 10 to 100 Å or so) thicknesses of metal and thereby preclude the formation of significant quantities of unwanted, less controllable sub-oxide films. Thermodynamic forces will drive the oxide compositions to their most stable, fully oxidized state, e.g., Nb₂O₅, Ta₂O₅, etc. As noted above, it will still be necessary to crystallize these duplex oxide layers. Such treatments can be done by RTP and will be shorter than those used on MOCVD and sputter-deposited oxides since the stoichiometry and purity of the "low temperature oxides" need not be adjusted at high temperature.

Please amend the paragraph beginning at page 31, line 17 as follows:

Some results have been obtained which demonstrate that at least a limited range of high temperature, super-conducting oxide films can be made by thermally oxidizing Y-Ba-Cu alloy films (~~see generally, Hase et al., "Method of manufacturing an oxide superconducting film," U.S. Pat. 5,350,738, Sept. 27, 1994~~). The present inventors have also disclosed how to employ "low temperature oxidation" and short thermal treatments in an inert ambient at 700C in order to form a range of perovskite oxide films from parent alloy films (see generally, J. M. Eldridge, "Low Cost Processes for Producing High Quality Perovskite Dielectric Films," application Serial No. _____). The dielectric constants of crystallized, perovskite oxides can be very large, with values in the 100 to 1000 or more range. The basic process is more complicated than that needed

to oxidize layered films of transition metals. (See Example III.) The TM layers would typically be pure metals although they could be alloyed. The TMs are similar metallurgically as are their oxides. In contrast, the parent alloy films that can be converted to a perovskite oxide are typically comprised of metals having widely different chemical reactivities with oxygen and other common gasses. In the Y-Ba-Cu system referenced above, Y and Ba are among the most reactive of metals while the reactivity of Cu approaches (albeit distantly) those of other noble metals. If the alloy is to be completely oxidized, then thin film barriers such as Pd, Pt, etc. or their conductive oxides must be added between the Si and the parent metal film to serve as: electrical contact layers; diffusion barriers; and, oxidation stops. In such a case, the Schottky barrier heights of various TM oxides and perovskite oxides in contact with various metals will help in the design of the tunnel device. In the more likely event that the perovskite parent alloy film will be only partially converted to oxide and then covered with a second layer of the parent alloy (recall the structure of Figure 2), then the barrier heights will represent that developed during oxide growth at the parent perovskite alloy/perovskite oxide interface. Obviously, such barrier heights cannot be predicted *ab initio* for such a wide class of materials but will have to be developed as the need arises. This information will have to be developed on a system-by-system basis.